

FINAL REPORT ON "REMOTE SENSING AND GEOCHEMISTRY OF PLANETARY
SURFACES", NAG5-10413

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INTRODUCTION

We have been examining the resources required to support potential life on Mars, as a way of understanding the possible abundance and distribution of life. Based on our understanding of the Earth, the necessary requirements for the environment to allow it to support life are (i) presence of liquid water, (ii) access to the biogenic elements (C, H, O, N, S, P, Ca, Fe, etc.), and (iii) a source of energy to drive chemical disequilibrium, such that the reactions back toward equilibrium can release energy to support metabolism. While even demonstrating that all of these requirements have been met would not mean that life would necessarily exist on Mars, they provide the context in which a search for life or analysis of geochemical characteristics that might be indicative of life might be carried out. Our previous work has focused on the first and third of these characteristics--determining where and when liquid water might have been present, and understanding the availability of chemical energy from weathering reactions that might support life.

In the analysis supported by this grant (covering the time period 2/15/01-2/14/02), we have been examining the second requirement--the abundance of the necessary biogenic elements, their geographical distribution on Mars and the information on the possible vertical distribution within the crust, and their geochemical accessibility and mobility within the crust and at the surface. In particular, our work during the performance period has emphasized phosphorous.

PHOSPHOROUS IN THE TERRESTRIAL ENVIRONMENT

Phosphorous is crucial for life on Earth, and presumably also would be for martian life. Without phosphorous, organisms simply could not exist, as it plays a major role in structural, signaling, and energetics of biological processes. For example, phospholipids are essential to cell membranes, making up the largest percentage of their molecules. Phosphate molecules also are involved with cell signaling processes, in that exchange of orthophosphate (PO_4^{3-}) moieties governs whether certain reaction cascades can proceed. And, phosphorous plays a major role in energetic processes because it is a part of adenosine triphosphate (ATP), the currency by which energy is traded in cells; when an anhydride bond between bound orthophosphate molecules breaks, it releases a packet of energy that can be coupled to fuel non-spontaneous chemical reactions in the cell.

Phosphorous is able to play these multiple roles in terrestrial biology for a variety of reasons:

(i) Phosphates are ionized and therefore cannot pass through cell membranes, which are essentially neutral. Consequently, phosphate molecules are effectively trapped inside cells.

(ii) However, the negative charge on phosphate molecules allows them to interact with positively charged molecules. These interactions are important in biochemical pathways where transient intermediate species are important.

(iii) Phosphate is somewhat resistant to hydrolysis, as the negative charge on phosphoesters (P-O bonds) repels the polar water molecule.

Poly- or pyrophosphates which are used by organisms are readily available in ecosystems on Earth from decaying organisms. Presumably, they would not have been available from similar sources at the time of the origin of life, and must have been made available entirely through geochemical means.

Polyphosphates such as P_4O_{10} form in a basaltic melt and then from evaporate from the surface of the melt. Hydrolysis can produce polyphosphates. Phosphate can either be dissolved in water or bound in phosphate minerals such as apatite. Under extreme conditions, some microbes can scavenge it from sedimentary apatite or even from apatite inclusions within silicates, despite the fact that apatite is practically insoluble.

PHOSPHATES ON MARS

The SNC meteorites show relatively high phosphorous abundances, some ten times greater than Earth relative to Si. Measurements at the Pathfinder landing site using the APXS showed values that, while still high, were closer to those of Earth. The greater abundance may be significant given that terrestrial biological and aqueous processes are able to redistribute phosphorous so that it is no longer a component in the crust; such processes may not be operating on Mars.

Phosphorous-bearing minerals can serve as both an indicator of the environment on Mars and as a possible biomarker. For example, analysis by Greenwood and Blake (2001) of the isotopic fractionation in O in PO_4 from ALH84001 and from Los Angeles show low fractionation values that are indicative of mineral formation in a high-temperature environment (in contrast to the high fractionation that occurs when formed in low-temperature environments mediated by biological activity). Similarly, the occurrence of apatite in environmental regimes in which whitlockite is the more-stable mineral form might be an indicator of the formation of apatite through biological means, as this is the result on Earth.

Our ongoing efforts have centered on trying to define the nature of processes in the martian environment that might affect phosphorous and what their implications would be for the abundance and distribution of phosphorous within the crust. We have constructed a data base for mineral reactions involving phosphorous, as input into standard thermodynamic models used to understand the stability of different minerals. Ultimately, the uncertainties in the abundance of P on Mars and in the environmental boundary conditions will make the results of such modeling somewhat uncertain, and the interpretation somewhat non-unique.

RESULTS OF ANALYSIS

Our results are summarized in the attached report that provides details on the above summary. The report was prepared by graduate student Sarah Earley as part of her research under this grant. Follow-on activity is being carried out at present, and is being supported by the follow-on grant (under a new grant number).

Phosphorus On Earth And Mars

Sarah Earley
20 November 2001

Introduction

Phosphorus is a required nutrient for life on Earth. The same would presumably be true for life on Mars. Studying the geochemical reactivity of phosphorus under conditions expected for Mars would tell us whether phosphorus is, or ever was, available for life on Mars. It would also tell us something about the geochemical conditions of the early Earth, since Earth and Mars were similar early in their history. Finally, phosphorus could feasibly be an effective biomarker when trying to determine whether samples from Mars contain evidence of past life. For these reasons, studying phosphorus on Mars is important.

This report outlines the topic of phosphorus on Earth and Mars, from the perspective of an astrobiologist. It contains the following information:

- Concise summary of the biology, chemistry, and geology of phosphorus on Earth
- Information that we know about Mars from past missions and the martian meteorites
- Detailed explanation regarding the importance of the research problem
- Proposed research and potential stumbling blocks
- Past research involving thermodynamic modeling
- Conclusions about the research problem

Phosphorus on Earth

Phosphorus is crucial for life on Earth. Without phosphorus, organisms would not exist, as phosphorus compounds play a major role in structural, signaling, and energetic biological processes. Phospholipids are essential to cell membranes, making up the largest percentage of their molecules. Phosphate molecules are also involved with cell signaling processes, in that exchange of orthophosphate (PO_4^{3-}) moieties governs whether certain reaction cascades proceed. Finally, phosphorus plays a major role in energetic processes because it is a part of adenosine triphosphate (ATP), the energy currency of cells (Lipmann, 1971). When an anhydride bond between bound orthophosphate molecules breaks, it releases a packet of energy that can be coupled to fuel non-spontaneous chemical reactions in the cell.

A look at phosphate chemistry provides an explanation as to the remarkable and unique chemical versatility of phosphorus in biological systems. According to Westheimer (1987), nature chose phosphates for several reasons.

1. Phosphates are ionized and therefore cannot pass through cell membranes, which are electrically neutral. Specifically, the lipid portion of the phospholipid is non-polar, so phosphates could not pass through them. Consequently, phosphate molecules are effectively trapped inside cells.
2. Moreover, the negative charge on phosphate molecules allows them to interact with positively charged molecules. This is a simple and effective molecular interaction. It is important in biochemical pathways where transient intermediates are key. Intermediate reactions cannot be long-lived for cellular pathways to proceed quickly.

- Another advantage of phosphate is that it is somewhat resistant to hydrolysis, as the negative charge on phosphoesters (P-O bonds) repels water, which is a polar molecule with a strong negative dipole. Conversely, anhydride bonds between phosphate molecules are not thermodynamically stable or kinetically inhibited, so biochemical reactions in which anhydride bonds are broken will take place in a reasonable time period. For example, when nucleotides combine to form DNA or RNA, they release inorganic phosphate, leaving behind one phosphate in the backbone of the nucleic acid. Figure 1 illustrates this process.

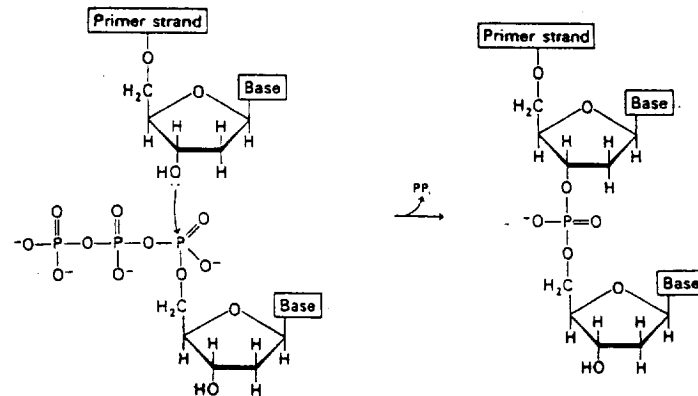


Figure 1. Formation of nucleic acids from individual nucleotides involves release of inorganic phosphate. When an anhydride bond breaks, it releases energy. (Figure from Stryer, 1995.)

Because of this chemical versatility and ubiquity, phosphorus plays a major role in life. If it were not available to organisms, life on Earth might not exist.

Polyphosphates are polymers of orthophosphate that might be of greater importance in biological systems than orthophosphate. For example, ATP, which has three orthophosphate components, is a polyphosphate molecule. In addition, the enzymes that bring phosphate into cells are specific for pyrophosphates (which contain two orthophosphate molecules). Even though orthophosphate is typically used for signaling, it is rarely found by itself in the cell. In fact, polyphosphate stores are often found in cells as granules (Jensen et al., 1976). Acid-soluble granules contain short chain polyphosphates, whereas acid-insoluble granules contain long chain polyphosphates. The short chain polyphosphates are more active metabolically—they readily (and reversibly) convert to orthophosphate. Poly- or pyrophosphates are readily available in ecosystems from decaying organisms. During the origin of life, they would presumably not be readily available. Only one mineral contains pyrophosphate, and it has never been found in nature; it is a wholly synthetic mineral.

There has been one study regarding a possible mechanism for polyphosphate production and release from volcanoes at the time of the origin of life (Yamagata et al., 1991). Polyphosphates such as P_4O_{10} form in a basaltic melt, and then evaporate from the surface of the melt. The extruded volcanic gases that contain the P_4O_{10} cool down rapidly and the P_4O_{10} partially

hydrolyzes, producing water-soluble polyphosphates. Yamagata et al. (1991) also pointed out that the primitive terrestrial atmosphere is thought to have formed by release of gas from the interior of the Earth. Polyphosphates would have been part of that gas. The polyphosphates would precipitate out of the gas, which would make them readily available for organisms on the early Earth. Recycling of the crust via subduction and subsequent volcanism would continually recycle the phosphate.

Although this is a plausible mechanism for a source of polyphosphate at the time of the origin of life, there could be other possibilities. Perhaps early in life's history, organisms obtained whatever form of phosphorus was available. If only orthophosphate were available, organisms could evolve the polymerization reactions required to make polyphosphate. Later on, when polyphosphates from decaying organisms become more abundant, organisms could have developed an efficient method for capturing the polyphosphates. Determining what processes occurred early in life's history is nearly impossible, since subsequent evolutionary pathways inevitably erased the earliest tenuous pathways.

These days, heterotrophs obtain nutrients by ingesting autotrophs. Autotrophs (primary producers) obtain phosphorus through phosphatases in their cell membranes that enzymatically pull in pyrophosphate from the surrounding external environment. It appears that the phosphate can either be dissolved in water or bound in phosphate minerals contained in rocks. When orthophosphate is scarce in groundwater, microbes scavenge it from sedimentary apatite or even apatite inclusions within silicates, despite the fact that apatite is practically insoluble. Research by Bennett et al. (2001) suggests that microbes make the environment at the mineral surface very reactive towards accelerated silicate dissolution, which frees phosphate contained within the silicate minerals. Microbes can make the mineral surface more reactive indirectly by modifying groundwater chemistry, or directly by altering mineral-water equilibria at the attachment site. Microbes can also accelerate mineral dissolution by producing acids and bases, organic ligands, extracellular polysaccharides, and enzymes. For example, silica dissolves more easily under basic conditions. Bennett et al.'s (2001) results are that microbes grown on surfaces of rocks that do not contain phosphate minerals do not thrive. When the rocks contain phosphate minerals, microbes will thrive. The trend is as expected: the more phosphate minerals that are in the rock, the more cell growth on the rock surface. This particular research is very recent, and much more work must be done in order to address the problem thoroughly. Moreover, the exact mechanisms by which the organisms are releasing and taking in phosphate are points of interest.

We also do not know whether the mineral in which phosphorus resides makes a difference. The experiments explained in the previous section involved apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$). Organisms could obtain phosphorus even though it was bound in the apatite matrix. If a different mineral were present, perhaps the phosphorus would not be as accessible to organisms. Though this does not seem too likely, biogeochemists have found that soil phosphorus trapped in complex organic molecules that do not dissolve or break down easily is effectively inaccessible to organisms. On the same principle, an insoluble phosphorus mineral may not release its phosphate readily enough for organisms to thrive on it.

Weathering of igneous and sedimentary rocks provides the most important source of phosphate that is not anthropogenic (Föllmi, 1996). Weathered phosphates are made bioavailable in soils, which act as temporary reservoirs of phosphate. In turn, the phosphate content of soil depends on the quality of the soil, the chemistry of the percolating groundwater, temperature, pH, Eh, and microbial activity. For instance, calcium-rich groundwater will immobilize phosphate, whereas sulfate-rich groundwater can mobilize phosphate.

Once weathering has occurred, the two main methods of phosphorus transport are water and wind. In water, phosphate will adsorb to colloidal iron and manganese oxyhydroxides, which can then act as transporters of phosphate in oxidized aqueous environments. Phosphate deposition occurs when the redox state of the environment changes, as phosphate does not adsorb to reduced iron or manganese oxyhydroxides. Wind is a second mode of transport for weathered phosphates. Wind carries a small but significant amount of phosphate particles, making up approximately 5% of mobilized phosphate (Föllmi and references therein, 1996). For instance, Saharan eolian input contributes a considerable amount of bioavailable phosphate in the Amazon tropical forest.

As previously mentioned, the phosphate used by the microbes came from apatite, which is the most abundant phosphate mineral on Earth. Other phosphate minerals include whitlockite ($\text{Ca}_9\text{MgH}(\text{PO}_4)_7$), struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), and crandallite ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$). These are secondary alteration minerals resulting from weathering, hydrothermal, and aqueous processes, typically derived from apatite. Apatite can also be formed from these minerals. It is thermodynamically favored, but not kinetically favored. As a result, minerals such as brushite, which nucleates faster than apatite despite being less thermodynamically stable, will form before apatite. Biomineralization often follows this trend.

Phosphorus on Mars

Since biological activity and aqueous processes are not predominant on Mars, we might assume that the behavior of martian phosphorus will be similar to that of phosphorus found in terrestrial environments in which inorganic processes dominate and liquid water is not readily available. Figure 2 shows that biogeochemical phosphorus cycles found on Mars will be limited as compared to those found on Earth.

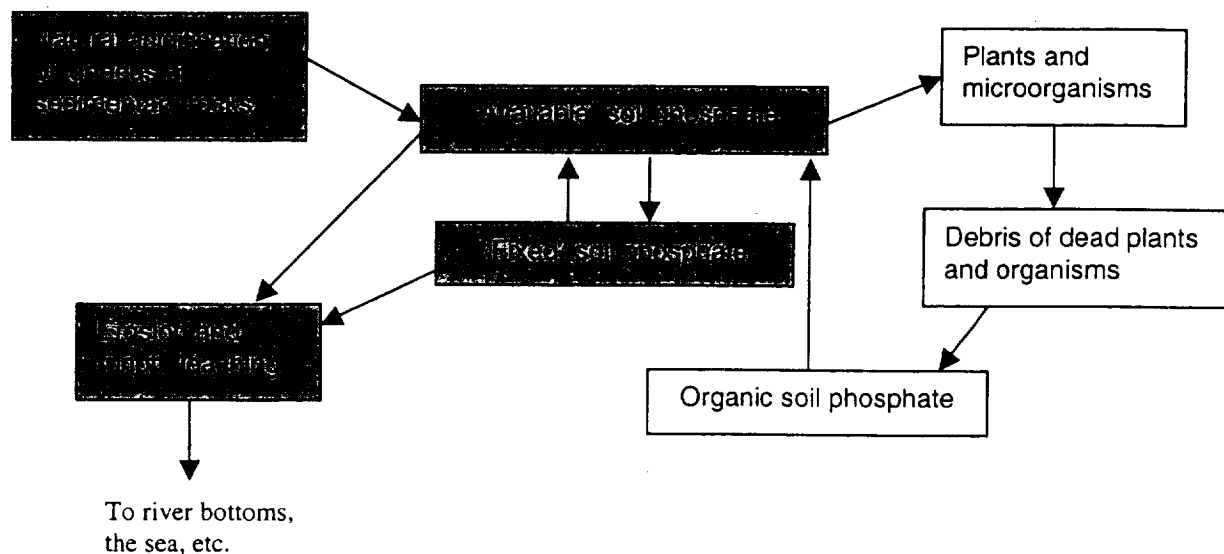


Figure 2. This figure illustrates the basic biogeochemical phosphorus cycles on Earth (adapted from Katchman, 1961). As far as we know, the phosphorus cycle on Mars includes only the components in the shaded boxes.

Such environments include the dry valleys of Antarctica and the Arctic. In fact, scientists consider these regions to be analogs of Mars, and have even gone so far as to build habitats to mimic those the might be built on Mars if humans ever settled there. Even these harsh environments have been found to contain some biological activity.

The geochemistry and mineralogy of the martian surface is known to some extent, but not really in detail. The basic petrology and mineralogy of the crust has been studied with Viking, Mars Pathfinder, Mars Global Surveyor, and will soon be studied with Mars Odyssey, but whether or not the martian crust contains significant amounts of the lower abundance minerals (such as carbonate minerals) has not yet been determined experimentally. Phosphate has garnered some attention, and some studies have been carried out to determine the concentration and mobility of phosphorus in the martian crust. Experimental data from Mars missions and the martian meteorites have provided some insight.

Initially scientists had thought that Mars contained much more phosphate on average than Earth, nearly 1% of the crust by weight on Mars versus 0.1% of the terrestrial crust (Wänke and Dreibus, 1988). The following diagram compares the relative element abundances of the martian and terrestrial mantles. According to the scientists, these are comparable to crustal abundances found in both planets.

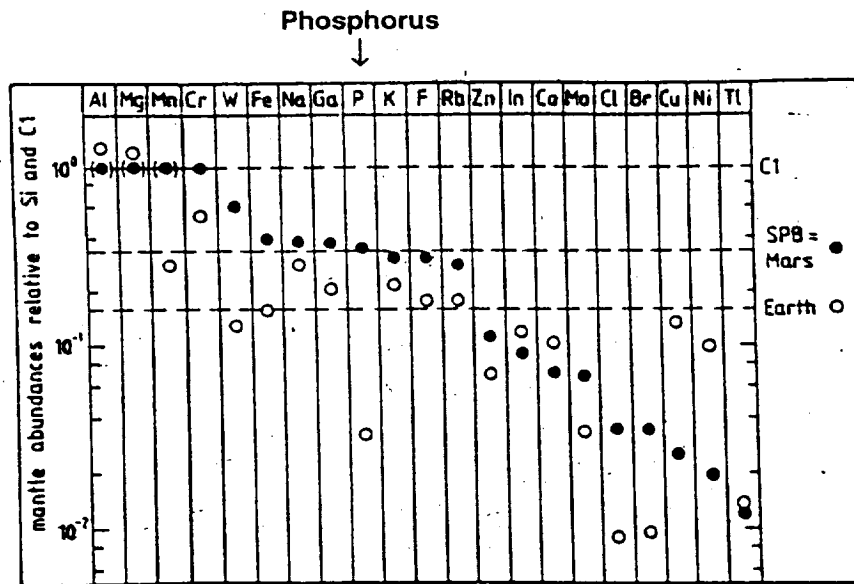


Figure 3. Comparison of elements found in the mantles of Earth and Mars as predicted by Wänke and Dreibus (1998).

Scientists had predicted these comparatively higher phosphorus concentrations on Mars because the SNC meteorites show high phosphorus concentrations. Dreibus et al. (2000) used a special peak fit method to analyze the alpha proton X-ray spectrometer (APXS) phosphorus data from the Mars Pathfinder. They found that the average abundance of phosphorus in the soils and rocks was only 0.5% by weight. Still high as compared to the average phosphorus abundance on Earth, but not that much higher considering that there are many terrestrial processes (e.g. biological and aqueous processes) that redistribute phosphorus so that it is no longer part of the terrestrial crust. The Earth's hydrosphere and biosphere contain phosphorus, thereby partially depleting the crust of phosphorus. Dreibus et al. (2000) also found that there were only small differences between the phosphorus concentration in martian soil and rock. This differs from the overall compositional trend found at the Mars Pathfinder landing site, where the soil was mafic and the rocks were andesitic. (One caveat of this research is that the uncertainty in the analyses can range from 10% to 40%, depending on background levels.) More recent research done by Brückner et al. (2001) involved better evaluation of the Mars Pathfinder APXS phosphorus data, based on recalibration of the instrument to take into account failure of shutter closure in front of the radioactive sources. According to this new research, the mean phosphorus abundance in both the soil and rock was approximately 0.4% by weight, which does not differ much from the earlier value of 0.5% phosphorus by weight.

The mobility of phosphorus in the martian crust is a second area of interest. Previously, Dreibus et al. (1996) carried out leach experiments on the SNC meteorites. The phosphates dissolved readily with dilute acids (HCl and HNO₃) at room temperature. The researchers also used an acidified (pH 3-4) brine solution containing MgSO₄ and found that the rare earth elements (REEs) and uranium dissolved, but that potassium did not. Potassium does not reside in phosphates, whereas REEs and uranium do. Their conclusions were that phosphates could be mobile within the Martian surface.

The petrologic processes that distributed phosphate throughout the martian crust probably differed from those on Earth, since Mars never had active plate tectonics. Even from a geochemical standpoint, the absence of extensive liquid water on Mars prohibits aqueous

processes from having the outstanding effect that they do on Earth. In addition, extensive biological activity on Earth plays a major role in distribution and availability of the biogenic elements on Earth. Lack of biological and aqueous activity on Mars means that certain elements, such as phosphorus, are not as mobile as they are on Earth. Yet, Dreibus and coworkers' research indicates that some process must be occurring to move phosphorus throughout the martian crust.

Dreibus et al.'s (2000) methods provide a glimpse into phosphorus concentration of the martian crust, and could be used for other low abundance elements in the future. The concentrations of low abundance elements in the martian meteorites have also been characterized. With respect to phosphorus, both apatite and whitlockite have been found in martian meteorites. The Shergottite meteorites contain whitlockite and accessory apatite, whereas the Chassigny and Nakhla meteorites contain only apatite (McSween, 1994). ALH84001 also contains phosphate minerals, as seen in the image below.

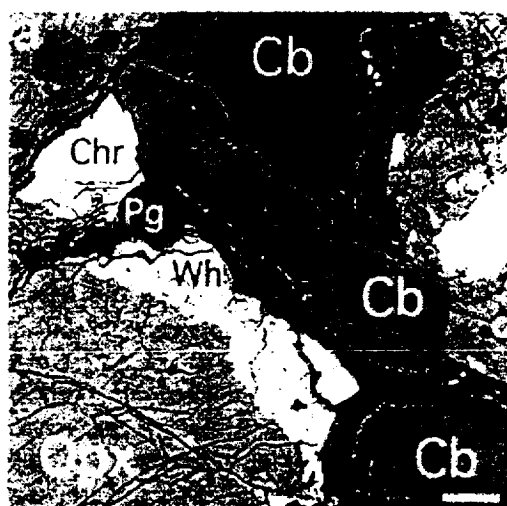


Figure 4. This backscattered electron image of ALH84001 shows that whitlockite grains are present (image from Greenwood et al., 2000). Whitlockite is denoted Wh, carbonate is Cb, and the unlabeled white rim of the black glassy material between the Wh and Cb grains is magnetite. This mineral assemblage suggests that the rock was hydrothermally altered.

However, there appears to be some debate as to whether ALH84001 contains apatite or whitlockite. Greenwood et al. (2000) claim that the phosphate mineral in ALH84001 is whitlockite (as shown in Figure 4 above), whereas Treiman (1995) and Mittlefehldt (1994) casually identify the phosphate mineral as apatite. Whether the phosphate mineral in ALH84001 is apatite or whitlockite is important since each would suggest different geochemical conditions. According to Elliott (1994), whitlockite will form in environments with particular Ca:Mg ratios (where Mg^{+2} concentrations are considerably higher), and favors slightly acidic environments. However, it can form within pH ranges of 5.5 to 9. The Mg^{+2} in the whitlockite structure

stabilizes the mineral from hydrolysis to apatite, and makes it more thermodynamically stable than apatite.

Much of the interest in which phosphorus minerals are in the martian meteorites derives from the idea that certain minerals will form only under certain geochemical conditions. Likewise, predicting some of the conditions to which a meteorite was exposed by looking at the end result is possible. Of course, only a limited amount of information about a meteorite's history is available, as some evidence will inevitably be erased as the meteorite is subsequently altered. The question as to whether the phosphorus mineral contained in the martian meteorites is whitlockite or apatite seems trivial but is very relevant because it provides insight into the meteorite's history, and consequently the parent body's history. Furthermore, even though thermodynamic calculations do not always provide completely accurate predictions as to which mineral will form in a particular system (kinetics play an important role as well), scientists have studied terrestrial phosphorus systems in great enough detail to know which phosphorus minerals will form under certain conditions.

Importance of this research

The research project that I chose involves the geochemistry of the biogenic element phosphorus within the martian crust. To my thinking, three main points illustrate the astrobiological importance of this problem:

- Without the necessary elements for life, life will not exist. Phosphorus is unequivocally necessary for life, as we know it. Similar assumptions can be made for life elsewhere.
- Early Mars was similar to the early Earth. However, plate tectonics and extensive weathering never occurred on Mars. By studying martian geochemistry we can get a sense of the conditions under which life on Earth originated nearly 4 billion years ago.
- Phosphate is a biomarker. The oxygen isotope ratios of phosphate can serve as a biomarker, and phosphate deposits containing carbon point to biological activity.

The problem is also important in a purely geochemical sense, as learning more about the geochemistry of the martian crust is a NASA goal unto itself.

Without the necessary elements for life, life will not exist.

One of the major questions in astrobiology is "Could life exist on Mars?" The necessary ingredients for life are thought to include liquid water, biogenic elements, and free energy. Whether these ingredients are or ever were available for life on Mars is still uncertain. Therefore, all of these areas are under intense scrutiny.

In addition to the ingredients being present, they must be accessible to organisms or life will not be able to thrive. Mixing of fluids in active hydrothermal systems is a source of free energy, but organisms must be able to harness the free energy. Likewise, there is water on Mars today, but since surface temperatures are so cold, the water is frozen. In both cases, the existence of the

ingredients does not matter because organisms cannot access them. We know that phosphorus exists on Mars; whether it is accessible to organisms is unknown. Geochemical modeling would help solve this problem by giving a first approximation about phosphorus on Mars.

Mars is similar to the early Earth.

Earth and Mars were similar early on, which suggests that the crustal composition of each was comparable. Unlike Earth, Mars has not changed much throughout time. Evidence of early Mars has not been significantly altered despite that today Mars is cold and harsh. Biogeochemical cycles on Earth are heavily influenced by biological activity, which practically determines the geological aspect of the cycles (see Figure 1). As far as we know, the same is not true of Mars. Studying Mars would give insight about the early Earth, and the conditions under which life originated nearly 4 billion years ago.

Phosphate is a biomarker.

Scientists do not yet know how to go about detecting life (or lack of life) using *in situ* analyses, or analyses of returned Mars samples. If life existed early on in Mars' history, signs of life would likely be very weak or even obliterated, since life is fairly fragile. As a result, detection of life could be extremely difficult. Scientists are trying to determine biomarkers that would be sufficient evidence for life. Phosphate could feasibly be a biomarker.

An orthophosphate molecule contains four oxygen atoms that can be isotopically heavy (^{18}O) or light (^{16}O). With the help of enzymatic catalysis, oxygen atoms from orthophosphate will exchange with oxygen atoms from water (in aqueous environments). In time, isotopic equilibrium will be reached. Oxygen isotope signatures of igneous apatite are similar to other high-temperature minerals on Earth, $\delta^{18}\text{O}_{\text{PO}_4}$ within 5.3‰ to 8‰ (Blake et al., 2001). However, low temperature (<80°C) biogenic phosphate in marine and hydrothermal environments has a different oxygen isotope signature, $\delta^{18}\text{O}_{\text{PO}_4}$ of approximately 20‰ to 25‰ (Blake et al., 2001). This considerable fractionation is the result of biology-mediated oxygen isotope exchange between water and phosphate in these relatively low temperature environments. To date no known inorganic processes cause this level of fractionation.

Applying the same premise to Mars, Greenwood and Blake (2001) analyzed grains of the phosphate mineral they call whitlockite from ALH84001 and the basaltic shergottite called Los Angeles. All of the grains had low $\delta^{18}\text{O}_{\text{PO}_4}$ signatures, indicating that the whitlockite formed in a high-temperature igneous environment. If phosphate from martian samples that are returned to Earth were found to have oxygen isotope signatures around 20-25‰, it would be powerful evidence that life exists on Mars, assuming that martian water and Earth water have similar oxygen isotope signatures. *In situ* analytical techniques might also benefit from incorporating oxygen isotope analyses when searching for life on Mars.

According to Mojzsis and Arrhenius (1998), certain phosphate minerals could be effective biomarkers. Whitlockite forms in sterile environments in both freshwater and marine environments with typical [Mg]:[Ca] ratios at pH values ranging from 6.5 to 8.5 (Mojzsis and

Arrhenius, 1998). At pH values higher than 8.5, apatite becomes thermodynamically stable, whereas whitlockite stability diminishes. Table 1 compares the primary phosphate minerals found in aqueous environments on Earth.

Mineral	pH condition of formation
Brushite	6-7.5
Whitlockite	7-9
Apatite	>8.5

Table 1. Phosphate mineral phases that form in sterile media of seawater composition (adapted from Mojzsis and Arrhenius, 1998)

As previously mentioned, apatite is the most abundant phosphate mineral on Earth, despite that it is not thermodynamically stable in many terrestrial environments. Mojzsis and Arrhenius (1998) believe that microbes are the cause of this prevalence, since microbes can control the kinetics of apatite formation by selectively nucleating apatite even when it is not thermodynamically stable. Therefore, they maintain that finding apatite in environments where whitlockite is actually the most the most stable phosphate mineral suggests biological control of the system. Obviously, finding out that apatite is the prevalent phosphate mineral on Mars would not necessarily signify the presence of past or present biological activity. Apatite is often found in igneous rocks that have not been exposed to microbial activity, so there must be non-biological mechanisms that result in apatite deposition. Igneous activity is one mechanism by which apatite forms.

Later in their 1998 article, Mojzsis and Arrhenius clarified that the presence of carbonate hydroxyfluorapatite in the stability field of whitlockite would be more suggestive of biological influence than apatite alone (provided that [Mg]:[Ca] values and pH could be determined independently). For instance, the Gunflint Chert is approximately 2.1 billion years old, and contains organic inclusions within apatite, which is present within siderite cores (Mojzsis and Arrhenius, 1998). The C:N:P ratio of the apatite grains within the chert is comparable to C:N:P ratios found in organisms today (120:16:1). Mojzsis and Arrhenius believe that this is evidence for life. The Gunflint chert also contains morphological evidence for life, which substantiates the chemical evidence. In addition, phosphate minerals in association with carbon that bears a biological isotope signature are even stronger evidence for life. Mojzsis et al. (1996) discovered carbon grains within apatite inclusions in early Archean sedimentary rock. When the scientists analyzed the carbon, they found that it has a carbon isotope ratio that is similar to what biological processes bring about. Though not definitive proof of life, these chemofossils present strong evidence that life may have existed as far back as 3.8 billion years ago. Mojzsis and colleagues proposed that similar studies should be conducted on Martian samples that would almost certainly lack unambiguous morphological evidence for life.

Proposed Research

Because the geochemistry of Mars cannot be studied in depth experimentally at this point, we must approach the problem in a different manner. In this case, theoretical modeling seemed to be

the most effective method for determining the behavior of phosphorus. We know that phosphorus is present within the martian crust, but we do not know the form in which it resides, or how mobile it actually is. The EQ3/6 software package performs thermodynamic calculations, which in turn allow one to study the geochemistry of a complicated system. Perhaps most importantly, it also allows one to study the wholly inaccessible geochemical systems of Mars.

In a nutshell, the research that I proposed to do involves 3 main aspects: compiling a thermodynamic database that includes the species of interest, running the models, and correctly interpreting the data for accurate results. Though determining model constraints makes the second aspect of the project questionable (for Mars is not well-constrained at this point), the first part turned out to be the real stumbling block.

What must be accomplished in order to get the project up and running properly is as follows. The EQ3/6 and SUPCRT databases must be modified so that they contain relevant species. SUPCRT is another thermodynamic program that allows one to calculate thermodynamic data for a variety of species at different temperatures and pressures (Johnson et al., 1992). The database requires a surprising amount of thermodynamic information, including obscure coefficients that are not normally found in thermodynamic tables. The EQ3/6 database requires equilibrium constants at different temperatures, information which SUPCRT can provide as long as its database is complete. Manually calculating equilibrium constants at various temperatures is possible, but only at limited temperature ranges and when enthalpy can be assumed to be constant. Calculating enthalpy changes (and therefore the other relevant thermodynamic variables) is also possible using the temperature-dependent heat capacity and integrating over the temperature range of interest, provided that the heat capacity is known and the thermodynamic information is first-rate. Thermodynamic tables from the literature are available as well (Robie and Hemingway, 1995; Vieillard and Tardy, 1984; Wagman et al., 1982). Two databases already included with the EQ3/6 software package contain a variety of aqueous phosphate species, but neither contains phosphate minerals or complexes. Heat capacity values can be found for the main phosphate minerals, though [accurate] heat capacity regression coefficients are much harder to find.

When adding species to the database, all the thermodynamic information must be "internally consistent." This means that the thermodynamic data for the species used to calculate Gibbs free energy, enthalpy, and entropy for a particular mineral must agree with the values already in the database for the same species. Therefore, any thermodynamic values obtained from the literature for a particular mineral must be checked to make sure they agree with the thermodynamic values for the aqueous phosphate species already in the database. The thermodynamic values for minerals that are calculated using thermodynamic values for aqueous phosphate species from the existing database typically do not agree with the literature values for phosphate minerals. This, added to the absence of thermodynamic data for the majority of the relevant phosphate minerals, made the task of compiling a worthwhile database difficult.

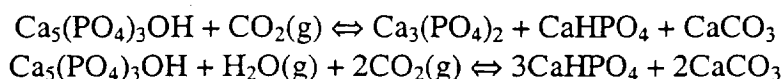
Running the models involves the following. First one must create an input file for EQ3NR, the speciation-solubility side of the EQ3/6 software package. The input file includes the concentrations of a variety of aqueous and mineral components, as well as the Eh, pH,

temperature, and a variety of instructions regarding mineral saturation states, activity coefficient options, and so on. The reason for running EQ3NR is to determine the speciation that will occur in a given system. A pickup file is written after each run, which can then be used as the EQ6 input file. EQ6 is the reaction path side of the EQ3/6 software package. It allows the user to model titration processes (e.g. fluid mixing), heating and cooling processes, and a variety of other factors. EQ3NR output represents a static system whereas EQ6 output contains the results from a dynamic system where at least one variable changes throughout the reaction path (Wolery, 1992; Wolery and Daveler, 1992). Ideally, the proposed research would have involved running models that were truly representative of martian systems, notably those systems that would feasibly contain minerals and aqueous species relevant to astrobiology.

Similar research conducted in the past was typically broader in scope. The only phosphate mineral that these studies considered was apatite, probably because it is the most abundant phosphate mineral on Earth. In retrospect, I think that if the proposed research were expanded to include the main phosphate species, and possibly the main carbonate, sulfate, and nitrate species, the project might be more feasible (since thermodynamic information is known for these species), and the results more informative.

Past Research involving thermodynamic modeling of Mars

As previously mentioned, the proposed research is not entirely new. There have been several studies with similar goals. James Gooding (1978) manually calculated thermodynamic stabilities of the primary minerals in mafic igneous rocks to learn about chemical weathering on Mars. (At the time he was doing the research, water in vapor and solid form had been detected on Mars. Although fluvial channels were known to exist on Mars, liquid water had not been detected. This is why Gooding focused primarily on gas-solid interactions rather than liquid-solid interactions.) He included apatite in the calculations, and considered the following chemical reactions:



The equilibrium constants (log K) for these reactions are -1181 and -1188 at 298 K, respectively. Breakdown of apatite due to weathering processes on Mars is not likely to occur. Gooding's results, which include both thermodynamic and kinetic considerations, indicate that apatite should be stable within the martian crust, unless first dissolved in liquid water. As a result, weathering products could be depleted in phosphorus.

Zolensky et al. (1987) proposed using EQ3/6 to study martian surface mineralogy as modified by aqueous alteration in a 1987 Workshop on Mars Sample Return Science. They assumed chemical equilibrium between the martian surface, atmosphere, and percolating groundwater. The goal was to model the weathering products produced by aqueous alteration. They constrained the input concentrations by making the assumption that the Shergottite meteorite and the martian crust are adequately similar. Zolensky et al. (1987) modeled both open and closed systems. A closed system resembles a stagnant system. Products are free to react with anything

in the system, and whatever precipitates out first might be lost as the system re-equilibrates to form new products. In an open system, precipitates are removed from the system so they can no longer react. An open system resembles an environment in which water flows through freely and transiently, removing products before they react again. Zolensky et al. (1987) ran their models at 2°C, since thermodynamic data for lower temperatures were not readily available. The results for both the open and closed systems were identical, with nontronite (a smectite clay), quartz, and calcite predominating the precipitating phases by the end of the reaction path. Hematite and gibbsite precipitated out immediately, and then re-dissolved very shortly afterward. Kaolinite precipitated out during the middle of the reaction path, re-dissolving toward the end. Sulfates and chlorides did not precipitate because the starting concentrations were too low. The figure shown below compares precipitation and dissolution of these minerals along the reaction path.

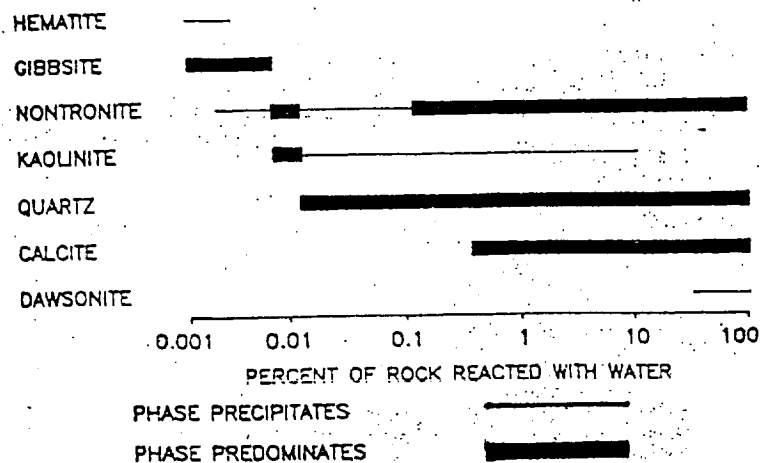


Figure 5. These are the results of thermodynamic modeling by Zolensky, et al. (1987). Lines pinch off where the minerals re-dissolve.

The researchers noted that nontronite typically forms in hot saline environments on Earth, as opposed to the cold non-saline environment in their model. A second point of interest is that calcite precipitated out in the modeled system, whereas carbonates have not been detected in martian soils. Unless the reaction path for aqueous alteration of Mars' surface proceeded only marginally (less than 1%), calcite should be apparent in sample measurements, according to these results. A third point of interest is that the closed and open systems yielded the same results. Zolensky et al. admit that the situation on Mars is more complicated than their models depict.

In another study, Plumlee et al. (1992) used the geochemical modeling programs CHILLER and SOLVEQ to model the surface mineralogy of an early warm wet Mars. They placed specific emphasis on apatite. The researchers assumed a temperature of 25°C in all models, which included 1) rainwater reacting with basaltic rocks, 2) formation of acid rain by volcanic gases, 3) reaction of acid rain with basaltic rocks, and 4) evaporation of water resulting from reactions

between rainwater and basaltic rocks. The rock composition was largely based on Chassigny parent magma. Plumlee et al. (1992) did not know the sulfur, chlorine, and phosphorus concentrations of this magma, so they assumed values based on terrestrial basalts (for S and Cl) and the parent magma of another SNC meteorite (P). They used a variety of different solutions, and varied conditions such as pH, oxygen fugacity, and carbon dioxide fugacity throughout the model runs. Plumlee et al. (1992) indicated that the most remarkable finding was that apatite formed during basaltic weathering, and that it could be a residence for chloride (in the form of chlorapatite). They do not state the importance of this finding.

These and a variety of other studies that involve modeling other aspects of Mars (Griffith and Shock, 1995; Griffith and Shock, 1997; McCollom and Shock, 1997; McCollom and Shock, 1998; McCollom, 1999) demonstrated that geochemical modeling of the martian crust could provide useful information regarding Mars. Geochemical modeling is worthwhile, so long as the models are carefully constructed. By modeling terrestrial systems for which experimental data are known, one could feasibly measure the accuracy of Mars models.

Conclusion

There is a paucity of information regarding phosphorus and the other biogenic elements on Mars at this point. Most of what we know comes from meteorite studies and the Mars Pathfinder APXS data. When done properly, thermodynamic modeling would contribute some more information about all the low-abundance species. We could then use the model results to evaluate potential landing sites on Mars that are relevant to astrobiology. If what we actually find at the landing sites differs from what geochemical models predict, we will need to determine whether the assumed environmental conditions are incorrect or if another factor, such as biological activity, is playing a role. The results might also tell us something about the geochemistry of the early Earth, as Mars and the early Earth were somewhat similar.

In the future, when sample return missions become feasible, we might be able to determine whether the biogenic elements exist in concert with one another in a manner that is indicative of biological processes. Mojzsis et al.'s (1996) discovery of carbon with $^{12}\text{C}/^{13}\text{C}$ isotope ratios reminiscent of those found for biological carbon found within apatite grains supports the notion that life existed on Earth as early as 3.8 billion years ago. If life on Mars only existed early on, and did not evolve the way it did on Earth, we might only find these types of chemofossils rather than morphological evidence. If so, phosphorus studies are of considerable importance.

However, the first step will be to determine larger scale geochemical signatures of the martian surface to determine whether environmental conditions that are conducive to life have ever existed on Mars. Places such as the walls of Valles Marineris or the sides of valley networks show layers that are reminiscent of deposits left behind as water evaporates. Hydrothermal systems are thought to be abundant and widespread on Mars, and are another environment that could foster life. Thermodynamic modeling is presently a feasible method with which we can study these environments. At the very least, it will provide a first approximation that will certainly be useful when more advanced Mars missions occur in the future.

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